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(54) Title of the Invention: Manufacturing Method of a Semiconductor Superlattice

(57) Abstract

Objective

The invention is related to a manufacturing method of a semiconductor superlattice of Ge layers and Si layers or Ge-Si layer and Si layers on an Si substrate, and the purpose is to make a practical heteroepitaxial growth method with satisfactory crystal quality and a rapid growth rate.

Constitution

The present invention comprises a semiconductor superlattice manufacturing method characterized by allowing Ge layers and Si layers or Ge-Si layers and Si layers to epitaxially grow on an Si substrate using the reduced pressure CVD method under an atmosphere wherein the amount of GeH_4 and oxide impurity gas contained is 100 ppb or less, and trisilane (Si_3H_8) is the source material gas with H_2 or an inactive gas as the carrier gas.

Figure of the relationship between the growth temperature and growth rate

Growth rate (Å/min)
Using Si_3H_8
Using Si_2H_6
Growth temperature (°C)

Claims

Claim 1

A semiconductor superlattice manufacturing method characterized by using a pressure reduction gaseous phase growth method to allow a germanium layer and a silicon layer or a germanium-silicon and a silicon layer to grow epitaxially on a silicon substrate under an atmosphere wherein the oxide impurity gas content is 100 ppb or less, and trisilane and germane are the source gases with hydrogen or an inactive gas as the carrier.

Claim 2

A semiconductor superlattice manufacturing method described in Claim 1 characterized by independently supplying trisilane gas and germane gas on the silicon substrate while interspersing the repeated growth of the aforementioned silicon layers and germanium-silicon layers with periods to stop the growth of the silicon layers and the germanium layers.

Claim 3

A semiconductor superlattice manufacturing method described in Claim 2 characterized by the composition ratio of the germanium in the aforementioned germanium-silicon layer being 50% or more.

Detailed Explanation of the Invention

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Field of Industrial Utilization

The present invention is related to a method to allow epitaxial growth at a high growth rate of a high quality semiconductor superlattice composed of silicon layers and silicon-germanium layers with a high composition ratio of germanium.

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A crystal in which germanium (called Ge hereinafter) and silicon (called Si hereinafter) are alternately grown epitaxially on an Si substrate having direct transition characteristics, and this is expected to be applied to optical elements.

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Materials that have been heteroepitaxially grown into ultra lattice crystals composed of Si and Ge have been used to develop devices for the purpose of high integration at ultra-high speed such as hetero bipolar transistors (HBT), light receiving elements, and high electron movement transistors (HEMT). The use of this method, which produces few crystalline faults and allows rapid growth, is extremely effective.

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Prior Art

Molecular beam epitaxy (MBE) is a method to form devices such as HBTs using a crystal layer that has been formed by allowing Si and Ge, or Si and Ge mixed crystal and Si, to grow epitaxially.

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Specifically, by using electron beam analysis to measure the signal strength and controlling the crystal growth rate on a molecular level, it is possible to conduct heteroepitaxial growth of a superlattice structure.

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Here, MBE is a technology that can grow crystals with extreme precision, but in practical terms there is a great fault density in the grown crystals, and there is the problem that the fault density must be controlled.

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In addition, it is not possible to process many large-scale substrates, and there is a productivity problem because of this. On the other hand, gaseous phase growth (CVD) is a method that can make a high quality crystal layer, but there is the problem that epitaxial growth of an Si layer or a mixed crystal layer with a large compositional ratio of Si is difficult at 500°C or less.

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Specifically, although it is possible to have growth at 500°C or less when using such methods as ultraviolet irradiation with special silanes such as fluorinated silane (SiF_2H_2), it is unknown if growth of crystal mixed with Ge is possible.

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Moreover, it is known that the boiling point of trisilane (Si_3H_8) is low at 52.9°C, and that it can be used as a material to form polycrystal Si and amorphous Si, but it is not known whether or not epitaxial growth is possible at low temperatures using CVD.

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In addition, it is known that, if the Ge layer is thick, Ge can be epitaxially grown on Si substrate using CVD, but because island-shaped growth is produced in the initial state of growth, a high density of lattice faults is included, and it is difficult to have crystal growth with a precise structure.

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Problems to Be Solved by the Invention

Germanes (GeH_4), such as germane (GeH_4), diethyl germane ($GeH_2(C_2H_5)$), and dimethyl germane ($GeH_2(CH_3)$) are most generally used as the source material gas to allow the epitaxial growth of Ge on Si substrate by CVD.

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Island-shaped growth easily occurs when conducting hetero growth on Si substrate, and therefore it is necessary to lower the growth temperature to 500°C or less in order to grow a Ge film with satisfactory smoothness.

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Next, if disilane (Si_2H_6) is used as a source material gas when allowing epitaxial growth of Si on Si substrate, although epitaxial growth is possible at 550°C or less, it is extremely difficult to conduct epitaxial growth at temperatures less than that.

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Moreover, when allowing heteroepitaxial growth of Si and Ge mixed crystals on Si substrates, although formation at temperatures of 550°C or more is possible when the Ge compositional ratio is small, it is difficult to grow a smooth mixed crystal layer when the Ge compositional ratio is large.

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From the above, it is necessary to lower the growth temperature of the Si layer to 500°C or less in order to form a semiconductor lattice by conducting epitaxial growth of Si layers and Ge layers or Si layers and Si-Ge mixed crystal layers.

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Means to Resolve the Problem

The aforementioned problems may be resolved through the configuration of a semiconductor superlattice manufacturing method characterized by using the reduced pressure CVD method to allow epitaxial growth of Ge layers and Si layers or Ge-Si layers and Si layers on an Si substrate in an atmosphere in which GeH_4 and oxide impurity gas has a content of 100 ppb or less using trisilane (Si_3H_8) as the source material gas and H_2 or an inactive gas as the carrier.

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Action

In order to grow a superlattice of an Si layer and a Ge layer on an Si substrate, or a superlattice composed of an Si layer and an Si-Ge mixed crystal layer, it is necessary to have a growth temperature of 500°C or less when forming an Si film using CVD as previously described, and the inventors have discovered that it is possible to use trisilane (Si_3H_8) gas and an atmosphere in which the oxide impurity gas (O_2, H_2O, CO, CO_2, etc.) content is 100 ppb or less.

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Figure 1 indicates the relationship between the growth temperature and the growth rate when using disilane (Si_2H_6) and trisilane (Si_3H_8). The Si_2H_6 partial pressure is 1.5×10^{-2} Torr, the Si_3H_8 partial pressure is 1×10^{-2} Torr and 2×10^{-2} Torr, and the total pressure with the H_2 carrier is 20 Torr. This figure indicates that, in contrast to the low growth rate of approximately 2 Å/min at 500°C when using Si_2H_6, there is high epitaxial growth of several to 10 Å/min at 500°C when using Si_3H_8, and it is even possible to have epitaxial growth at 450°C.

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Further, when conducting experiments of epitaxial growth using Si_3H_8, we found that it was necessary to have an extremely small content of oxide impurity gases such as O_2, H_2O, CO, and CO_2 at a level of 100 PPB or less, and for that reason, the reduced pressure CVD device used must have the conditions of high gas density, and highly pure carrier gas, Si_3H_8, and GeH_4.

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Further, we observed that when the partial pressure of Si_2H_6 and Si_3H_8 is 4×10^{-2} Torr or more, polycrystals are grown on the substrate surface. Next, Figure 2 indicates the results of experiments to investigate the relationship between superlattice cycles and the flow rate of GeH_4 gas derived from x-ray analysis measurements that were measures taken at a low analytic angle of 0° to 20°. The square marks indicate the situation when the substrate temperature is 470°C, the Si_3H_8 supply rate is 100 ml/min, the supply time is 120 seconds, and the GeH_4 supply time is 30 seconds. The circle mark indicates the situation when the substrate temperature is 550°C, the Si_2H_6 supply rate is 20 ml/min, the supply time is 30 seconds, and the GeH_4 supply time is 10

seconds. The triangle mark indicates the situation when the substrate temperature is 500°C, the Si_2H_6 supply rate is 40 ml/min, the supply time is 120 seconds, and the GeH_4 supply time is 20 seconds.

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Here, the white marks indicate the measured results, and that superlattice growth has occurred, and the black marks indicate that no superlattice cycle was found. Here, no small and no large growth cycles were observed, and the reason is that when the growth cycles are small, the Ge layer is in the form of a mixed Si-Ge crystal, and when the growth cycle is large, the surface is extremely rough because the Ge has grown in an island shape, and in terms of appearance it is similar to a mixed crystal.

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According to this figure, no cycle was observed at 6 Å or less and 20 Å or more at superlattice 4 expressed by the circle marks, in which Si_2H_6 was used and the growth temperature was 550°C. No cycle was observed at 4 Å or less and 30 Å or more at superlattice 5 expressed by the square marks, in which Si_3H_8 was used and the growth temperature was 470°C. It was found that the range of the cycle width could be broadened by using Si_3H_8.

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Moreover, based on the mean composition of the SiGe superlattice that was derived from the results of the x-ray analysis of the surface (004), the Ge composition ratio within the Ge layer was rather high at 50% at superlattice 4 expressed by the circle marks, in which Si_2H_6 and GeH_4 were used and the growth temperature was 550°C, and at superlattice 6 expressed by the triangle marks, in which the growth temperature was 500°C. However, it was estimated that the Ge composition in the Ge layer was 80% or more at superlattice 5 expressed by the square marks, in which Si_3H_8 and GeH_4 were used and the growth temperature was 450°C. This was understood to be a notable improvement.

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Embodiments

Embodiment 1: (Example of Multi-Layer Growth of Ge Layers and Si Layers)

Si with a surface grade (001) was taken as a substrate, and the surface was treated with oxide by immersing this in a mixed solution of sulfuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2). Then, immersing in hydrofluoric acid (HF) solution and washing removed the oxide film. Next, this substrate was loaded into a gaseous phase growth device, and as pre-processing, the oxide was removed by heat processing for 10 minutes at a temperature of 900°C in an atmosphere of highly pure H_2 and a vacuum of 10 Torr.

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Thereafter, the temperature was cooled to 450°C, and Si and Ge layers were alternately grown by alternately supplying Si_3H_8 and GeH_4 with a partial pressure of 2×10^{-2} Torr respectively and H_2 with a total pressure as a carrier of 20 Torr, and a superlattice was formed.

Embodiment 2: (Example of Growth of Ge-Si Layers and Si Layers)

After the Si substrate was washed and the oxide film eliminated in the same manner as in Embodiment 1, GeH_4 and Si_3H_8 gases were independently supplied for short periods of time based on the gas supply program indicated in Figure 3.

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Specifically, after supplying GeH_4 for 1 minute, a 20-second gap was left, and then Si_3H_8 was supplied for 4 minutes. Then, a 20-second gap was provided and GeH_4 was then supplied for 1 minute, and this was repeated. When the GeH_4 supply time is shortened in this way, it is possible to make a mixed crystal layer with a thickness of several Å because the composition is made smooth by the alternate dispersion of Ge and Si.

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In addition, an Si layer can be made by supplying Si_3H_8 up to a time equivalent to the thickness. A superlattice can be produced by the above method.

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Effects of the Invention

According to the embodiments of the present invention, it is possible to allow satisfactory growth quality at a high growth rate of a superlattice structure composed of Ge layers and Si layers or Ge-Si mixed crystal layers containing a high concentration of Ge and Si layers.

Brief Explanation of the Figures

Figure 1 is a figure of the relationship between the growth temperature and growth rate.

Figure 2 is a figure of the relationship between the GeH_4 flow rate and the superlattice cycles.

Figure 3 is an embodiment of the gas supply program to form a superlattice structure.

Figure 1 Figure of the relationship between the growth temperature and growth rate

Growth rate (Å/min)
Using Si_3H_8
Using Si_2H_6

Growth temperature (°C)

Figure 2 Figure of the relationship between the GeH_4 flow rate and the superlattice cycle

Superlattice cycle (Å)
GeH_4 flow rate (ml/min)

Figure 3 Embodiment of a gas supply program to form a superlattice structure

Supply rate
Supply time (min)